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OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: EXTRACTION AND ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS BY DFLM01.0, INCLUDING REVISION DFLM01.1 (SEPTEMBER 1991) AND METHOD 8280A

(SUPERSEDES: SAC-ID-0011, REVISION 1.0, APRIL 10, 1998)

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1. SCOPE AND APPLICATION

1.1. This method is appropriate for the extraction and determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soil, sediment, fly ash, and chemical waste samples. The analytical method requires the use of high resolution gas chromatography and low resolution mass spectrometry on sample extracts that have been subjected to specified cleanup procedures.

1.2. The calibration range is dependent on the compound and sample size. The sample size varies by sample matrix. The upper limit of the calibration range for each is compound is 20 times the Contract Required Quantitation Limits (CRQLs). See TABLE 1 for list of compounds and their CRQLs.

1.3. Analysis time takes approximately 50 minutes for a GC/MS run.

1.4. Typically, the lowest calibration standard is used as the reporting and flagging limit. See Table 4, standard CC1.

2. SUMMARY OF METHOD

2.1. Soil/Sediment Extraction

2.1.1. A 10 g aliquot of soil/sediment sample is spiked with the internal standard solution and extracted with toluene in a combination of Soxhlet extractor and a Dean Stark water separator (SDS).

***NOTE:** The sample should not contain an obvious liquid phase. If an obvious liquid phase exists, notify the project manager for consultation with the client.*

2.2. Water Extraction

2.2.1. Approximately 1 L of the water sample is spiked with the internal standard solution and filtered to separate the aqueous and particulate fractions. The filtered aqueous fraction is extracted with methylene chloride using a separatory funnel. The particulate fraction is extracted with toluene in a SDS extractor. The extracts of the two fractions are combined for cleanup.

***NOTE:** Multiple phases should not be present. Consult with the client if multiple phases are present.*

2.3. Fly Ash Extraction

2.3.1. A 10 g aliquot of the fly ash is washed with dilute hydrochloric acid, spiked with the internal standard solution, and extracted with toluene in a SDS extractor.

NOTE: *The sample must not contain an obvious liquid phase.*

2.4. Chemical Waste Sample Extraction

2.4.1. A 1g aliquot of stillbottom/oil/oily sludge/oil-laced soil sample is spiked with the internal standard solution and extracted with toluene in a combination of Soxhlet extractor and a Dean Stark water separator (SDS).

2.5. Cleanup

2.5.1. Immediately prior to cleanup, all extracts are spiked with a ^{37}Cl-2,3,7,8-TCDD standard. The addition of this standard differentiates between losses of analytes or internal standards during extraction and losses that occur during the various cleanup procedures.

2.5.2. The extracts are subjected to an acid-base washing treatment and dried. Following a solvent exchange step, the extract is cleaned up by a column chromatographic procedures including: silica gel, acid alumina, and charcoal/silica columns, to eliminate sample components that may interfere with the detection and measurement of PCDDs/PCDFs. The extracts are concentrated and the solvent is exchanged to tetradecane. The recovery standards are added to a 50 µL aliquot of the extract and the aliquot is reduced to a final volume of 50 µL. The remaining 50 µL of extract is retained in the event that dilutions or reanalysis are required.

2.6. Analysis

2.6.1. A 2 µL aliquot is injected into a fused silica capillary column in a gas chromatograph (GC) interfaced to a mass spectrometer (MS). Identification of PCDDs/PCDFs is based on the detection of the ions specified in TABLE 2, and the measurement of the appropriate relative abundance (ratio) of two characteristic ions in the molecular ion cluster. The PCDDs/PCDFs are quantitated by comparing the MS response of the detected analyte relative to the MS response of the appropriate internal standard.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

3.2. Soil/Sediment Sample: A portion of wet soil/sediment, which does not contain an obvious liquid phase.

3.3. Water Sample: A single phase system that is primarily clean water but may contain very small amounts of floating, suspended, and settled particulate matter.

3.4. Fly Ash Sample: A solid matrix from an incineration or other combustion process, which may contain water and other solids.

3.5. Chemical Waste Sample: Sample matrices of oils, stillbottoms, oily sludge, oil-laced soil, and surface water heavily contaminated with the matrices mentioned previously.

3.6. Concentration Calibration Solution (TABLE 4): Solutions (tetradecane) containing known amounts of selected analytes, five internal standards and two recovery standards that are analyzed prior to sample analysis. The solutions are used to determine the ratio of the instrument response of the analytes to that of the appropriate internal standard and the internal standards to that of the recovery standards.

3.7. Internal Standards (TABLE 8): 13C-2,3,7,8-TCDD, 13C-1,2,3,6,7,8-HxCDD, 13C-OCDD, 13C-2,3,7,8-TCDF and 13C-1,2,3,4,6,7,8-HpCDF (in isooctane) are added to every sample and are present at the same concentration in every blank, quality control sample, and concentration calibration solution. The internal standards are added to the sample before extraction and are used to measure the concentrations of the analytes.

3.8. Recovery Standard (TABLE 8): 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD are added to every blank, quality control sample, and sample extract aliquot prior to analysis. Recovery standards are used to measure the recovery of the internal standards.

3.9. Cleanup Standard: ^{37}Cl-2,3,7,8-TCDD is added to every sample, blank, quality control sample, and concentration calibration solution. It is added to the samples after extraction but prior to cleanup.

3.10. Response Factor: The ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of an internal standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used in the quantitation calculations.

3.11. Signal-to-noise: The ratio of analyte signal to random background signal.

3.12. Estimated Detection Limit (EDL): The concentration of an analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The EDL is calculated for each 2,3,7,8-substituted isomer for which the response of the quantitation and confirmation ions is less than 2.5 times the background level. (See TABLE 1 Reporting Limits).

3.13. Estimated Maximum Possible Concentration (EMPC): The concentration of a given analyte that would produce a signal with a given peak area. The EMPC is calculated for 2,3,7,8-substituted isomers for which the quantitation and/or the confirmation ion(s) has signal-to-noise in excess of 2.5 but does not meet all of the other identification criteria.

3.14. Window Defining Mix: A solution which contains the first and last eluting isomer of each homologue and is used to verify that the switching times between the descriptors have been properly set.

3.15. Homologous Series: A series of organic compounds in which each successive member has one more atom or group of atoms than the preceding member.

3.16. Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.17. Congener: Any member of a particular homologous series, for example, pentachlorinated dibenzofurans.

3.18. Continuing Calibration Solution (Daily Standard): A solution analyzed every 12 hours to demonstrate continued acceptable GC/MS performance. The solution is the same as the Mid-Level concentration calibration solution, CC3.

3.19. Column Performance Check Mixture (CPSM): A mixture of TCDD isomers (including the 2,3,7,8-TCDD isomer) known to elute near each other on an SP-2331 column. This mixture demonstrates acceptable resolution between the 2,3,7,8-TCDD isomer and all other TCDD isomers on the SP-2331 column (valley $\leq$ 25%).

4. INTERFERENCES

4.1. Sample components may interfere with the detection and measurement of PCDDs/PCDFs. To eliminate interference, the extract is cleaned up by column chromatographic procedures.

4.2. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, which may cause misinterpretation of chromatographic data. All of these materials shall be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

NOTE: Analysts must avoid using PVC gloves due to the possibility of contamination.

4.3. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be necessary.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL Sacramento associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. N-Dex nitrile gloves provide varying degrees of intermittent splash protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: Methylene chloride, dibenzo-p-dioxins and dibenzofurans. 2,3,7,8-TCDD is a carcinogen, teratogen, and mutagen. Other PCDDs and PCDFs with chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. Exposure to these chemicals must be kept to a minimum by whatever means available. Methylene chloride.

5.3.2. The following materials are known to be **flammable**: Methanol, Toluene, Hexane, Acetone, isooctane, cyclohexane.

NOTE: Methanol will readily absorb via the skin.

5.3.3. The following chemical is known to be a **neurotoxic agent:** Hexane.

5.3.4. The following chemicals are known to be **corrosive:** Sodium hydroxide, sulfuric acid, hydrochloric acid.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL Sacramento associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Material Safety Data Sheets (MSDSs) are available to lab personnel, and must be read before samples or chemicals are handled.

6. EQUIPMENT AND SUPPLIES

6.1. Filters

6.1.1. Glass wool, rinsed with methylene chloride

6.1.2. Glass fiber filter: 15 cm, used with Buchner funnel

6.1.3. Whatman #1 (or equivalent)

6.1.4. White quartz sand. 60/70 mesh, used in the SDS extractor.

6.2. Glass wool, silanized.

6.3. Miscellaneous clean glassware

6.4. Dean Stark Water Separator Apparatus.

6.5. Concentrator tubes, 15 mL conical centrifuge tubes.

6.6. Separatory funnels, 500 mL and 2 L separatory funnels with a Teflon stopcock.

6.7. Soxhlet apparatus, 500 mL flask, all glass - Complete with glass extractor body, condenser, heating mantle and variable transformer for heat control.

6.8. Boiling chips

6.9. Buchner funnel, 15 cm

6.10. Filtration flask, 1 L capacity

6.11. Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS) - Microcmass magnetic sector VG/Autospec or equivalent.

6.11.1. The GC must be capable of temperature programming and equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port is designed for capillary columns; a splitless or an on-column injection technique is recommended.

6.11.2. The mass spectral data is obtained by using a low resolution instrument, utilizing 70 volts (nominal) electron energy in the electron impact mode. The system is capable of selected ion monitoring (SIM) for at least 18 ions simultaneously, with a cycle time of 1 second or less. Minimum integration time for SIM is 25 millisecond per m/z. The integration time used to analyze samples is identical to the time used to analyze the calibration solutions and QC samples. Total data acquisition time per cycle (18 ions) must not exceed 1 second.

6.11.3. An interfaced data system is present to acquire, store, reduce, and output mass spectral data.

6.11.4. GC Columns:

6.11.4.1. Fused silica capillary columns are required. The columns shall demonstrate the required separation of all 2,3,7,8-specific isomers whether a dual column or a single column is chosen. Column operating conditions shall be evaluated at the beginning and end of each 12 hour period during which samples or concentration calibration solutions are analyzed.

6.11.4.2. Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on the 60 m DB-5 column. In order to determine the concentration of the individual 2,3,7,8-substituted isomers, if the toxicity equivalence is greater than 0.7 ppb (solids), 7 ppt (aqueous), or 7 ppb (chemical waste), the sample extract shall be reanalyzed on a 60 m SP-2331 (or equivalent) GC column.

6.11.4.3. For any sample analyzed on a DB-5 (or equivalent) column in which either 2,3,7,8-TCDD or 2,3,7,8-TCDF is reported as an Estimated Maximum Possible Concentration, regardless of TEF-adjusted concentration or matrix, analysis of the extract is required on a second GC column which provides better specificity for these two isomers.

6.11.4.4. **For Method 8280A, the following conditions may require second column analysis:** *Second column analysis is dependent upon client requirements and site history.*

1) The criteria listed in Section 6.11.4.2 must be met and 2,3,7,8-TCDF must be detected or reported as an EMPC, or

2) If 2,3,7,8-TCDF is reported as an EMPC that is above the quantitation limit for the matrix.

7. REAGENTS AND STANDARDS

7.1. Solvents

7.1.1. High purity, distilled-in-glass: hexane, methanol, methylene chloride, toluene, isooctane, cyclohexane, acetone, tetradecane.

7.2. Sodium Sulfate: granular, anhydrous

7.2.1. Rinse with methylene chloride.

7.3. Sodium Hydroxide, ACS grade

7.3.1. Prepare a 10N solution in distilled water.

7.4. Sulfuric Acid, concentrated ACS grade, specific gravity 1.84

7.5. Hydrochloric Acid, concentrated ACS grade, specific gravity 1.17.

7.5.1. Prepare a 1N solution in distilled water for pretreatment of fly ash samples.

7.6. Column chromatography reagents

7.6.1. Alumina, acidic: ICN activated AA, Super I, ICN Biomedical or equivalent

7.6.2. Activated Charcoal: EM Science.

7.6.3. Silica gel: High purity grade Kiesel Gel 60, 70-230 mesh

7.6.3.1. Activate for up to 12 hours at 190°C before use. Store at 190°C in a covered flask.

7.6.4. Charcoal/Silica gel

7.6.4.1. Mix 5.0 g charcoal and 95 g activated silica gel. Activate mix for 12 hours at 190°C before use. Store at 190°C in a covered flask.

7.6.5. H_2SO_4 Silica gel

7.6.5.1. Mix 24 mL (44g) concentrated H_2SO_4 and 56g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.6.6. NaOH/Silica gel

7.6.6.1. Mix 34 mL 1N NaOH and 67g activated silica gel. Stir and shake until free flowing. Store at room temperature.

7.7. Calibration Solutions

All PCDD/PCDF calibration, internal standard, clean-up recovery standards, and spiking solutions are stable for one year from preparation. After one year, solutions may be revalidated. The revalidated solution may be used for an additional year or until there is evidence of compound degradation or concentration. The revalidation must be performed using an unexpired, not previously validated solution from a second lot or second vendor.

7.7.1. Five tetradecane solutions (CC1-CC5) containing 10 unlabeled and 7 carbon-labeled PCDDs/PCDFs at known concentrations are used to calibrate the instrument. One of these five solutions (CC3) is used as the continuing calibration solution and contains 7 additional unlabeled 2,3,7,8-substituted isomers that are commercially supplied. The concentration ranges are homologue-dependent with the lowest concentrations associated with tetrachlorinated dioxins and furans (0.1-2.0 ng/µL), and higher concentrations associated with the penta- through octachlorinated homologues (0.5-10.0 ng/µL).

7.8. Internal Standard Solution

7.8.1. The solution contains the five internal standards in isooctane at the nominal concentrations listed in TABLE 8.

7.9. Recovery Standard Solution

7.9.1. The isooctane solution contains the recovery standards, 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD, at concentrations of 0.5 ng/µL.

7.10. Continuing Calibration Solution

7.10.1. A solution containing standards to be used for the identification and quantitation of target analytes (CC3).

7.11. Window Defining Mix

7.11.1. A solution obtained by the laboratory through a commercial vendor. This solution contains the first and last eluting isomer of each homologue (See TABLE 6) and is used to verify that the switching times between the descriptors have been properly set.

7.11.2. The window defining mix need not contain any of the labeled internal or recovery standards, as no quantitative measurements are based on this mixture.

7.12. Cleanup Standard

7.12.1. A solution containing ^{37}Cl-2,3,7,8-TCDD at concentration of 0.25 ng/µL (0.25 µg/mL) in isooctane and is added to all sample extracts prior to cleanup. The recovery of this compound is used to judge the efficiency of the cleanup procedures.

7.13. Matrix Spiking Standard

7.13.1. A solution containing 10 of the 2,3,7,8-substituted isomers at the concentrations listed in TABLE 7 in isooctane, and is used to prepare the spiked sample aliquot. Dilute 50 µL of this standard to 1.0 mL with acetone and add to the aliquot chosen for spiking.

7.14. Column Performance Solution

7.14.1. The laboratory obtains this solution through commercial vendors. The solution contains 2,3,7,8-TCDD and the other TCDD isomers (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair) that elute closest to 2,3,7,8-TCDD on the SP-2331 (or equivalent) GC column. The concentrations of these isomers should be approximately 0.5 ng/µL in tetradecane.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Water Samples

8.1.1. Each water sample received will consist of at least two 1-liter (or quart) amber glass bottles. Store at 4 ± 2°C from collection until extraction. Do not freeze. After a portion of the sample is removed for analysis, the unused portion of the sample is stored at 4 ± 2°C in a locked, limited access area for at least 60 days from the date of data submission.

8.2. Soil/Fly Ash/Chemical Waste Samples

8.2.1. Each soil/fly ash/chemical waste sample received will be contained in a 1-pint glass jar. Until a portion is removed for analysis, the sealed sample must be stored in a locked, limited access area at room temperature. Do not freeze. After a portion is removed for analysis, the unused portion of the sample is returned to its original container and stored at room temperature for at least 60 days from the date of data submission.

8.3. Protect samples from light at the time of receipt until extraction to minimize the potential for photodecomposition.

8.4. **For Method 8280A:**

8.4.1. All samples should be stored at $4^{o\pm}$ 2° C in the dark, for at least 30 days from the date of data submission, extracted within 30 days of collection and completely analyzed within 45 days of extraction. Whenever samples are analyzed after the holding time expiration date, the results should be considered to be minimum concentrations and should be identified as such.

NOTE: *The holding times listed in Section 8.4.1 are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed in Section 8.4.1 may be as high as a year for certain matrices. Sample extracts, however, should always be analyzed within 45 days of extraction.*

9. QUALITY CONTROL

9.1. One method blank must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The method blank is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when target analytes are detected in the method blank above the reporting limit or when internal standard recoveries are outside control limits. Re-extraction of the blank, other batch QC, and the affected samples are required when the method blank is deemed unacceptable. See STL Sacramento QA Policy 003 for specific acceptance criteria.

9.2. A Laboratory Control Sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water, Ottawa sand, sodium sulfate, etc.) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, other batch QC and all associated samples are required if the LCS is deemed unacceptable. See STL Sacramento QA Policy 003 for specific acceptance criteria.

9.3. A Matrix Spike and Duplicate Analysis (MS and DU) set must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. A MS is an aliquot of a selected field sample spiked with analytes of known identity and concentration. The MS and duplicate set must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside control limits must be within control limits in the LCS. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spike analyte is outside control limits provided on the LIMS or by the client. Re-extraction of the blank, an LCS, the selected field sample, the MS and DU may be required after evaluation and review.

9.3.1. **For Method 8280A:** A Matrix Spike and Matrix Spike Duplicate set must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples.

9.4. A duplicate control sample (LCSD or DCS) must be substituted when insufficient sample volume is provided to process an MS/DU or MS/MSD set. The LCSD is evaluated in the same manner as the LCS. See STL Sacramento QA Policy 003 for specific acceptance criteria.

10. CALIBRATION AND STANDARDIZATION

10.1. Mass Calibration

10.1.1. Mass calibration of the mass spectrometer is recommended prior to analyzing the continuing calibration solution or samples each day. It is desirable to tune the instrument to greater sensitivity in the high mass range to achieve better response to the later eluting compounds. (See Appendix II for instrument tuning instructions.)

10.2. Window Defining Mix (WDM)

10.2.1. Prior to the calibration of the GC/MS system, it is necessary to establish the appropriate switching times for the SIM descriptors and to verify the chromatographic resolution. The switching times are determined by the analysis of the window defining mix, which contains the first and last eluting isomer in each homologue. (See TABLE 6)

10.2.2. The window defining mix must be analyzed at the following frequency:

10.2.2.1. Before initial calibration or the initial continuing calibration on each instrument and GC column used for analysis.

10.2.2.2. Each time a new initial calibration is performed, regardless of reason.

10.2.2.3. Each time adjustments or instrument maintenance activities are performed that may affect retention times.

10.2.2.4. Any time the retention time of either 13C-1,2,3,4,-TCDD or 13C-1,2,3,7,8,9-HxCDD recovery standards, in <u>any</u> analysis, varies by more than 10 seconds from its retention time in the most recent continuing calibration standard. **For Method 8280A, this section is not applicable.**

10.3. Chromatographic Resolution

10.3.1. For analyses on a DB-5 (or equivalent) GC column, the chromatographic resolution is evaluated by the analysis of the CC3 standard during both the initial and continuing calibration procedures.

10.3.2. For analyses on an SP-2331 (or equivalent) GC column, the chromatographic resolution is evaluated before the analysis of any calibration standards by the analysis of a commercially available column performance mixture that contains the TCDD isomers that elutes most closely with 2,3,7,8-TCDD on this GC column (1,4,7,8-TCDD and the 1,2,3,7/1,2,3,8-TCDD pair).

10.3.2.1. Analyze a 2 µL aliquot of this solution, using the column operating conditions and descriptor switching times previously established.

10.3.3. GC Resolution Criteria for SP-2331 or equivalent column. The chromatographic peak separation between unlabeled 2,3,7,8-TCDD and the peaks representing all other unlabeled TCDD isomers shall be resolved with a valley of $\leq$ 25%

$$\text{Valley} = \frac{X}{Y} \times (100)$$

Where:

X=the distinction from the baseline to the bottom of the valley between adjacent peaks.

Y=the peak height of any isomer.

10.3.3.1. The resolution criteria must be evaluated using measurements made on the selected ion current profile for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

10.3.3.2. Further analyses must not proceed until the GC resolution criteria have been met.

10.3.4. GC Resolution for DB-5 or equivalent column. The chromatographic peak separation between 13C-2,3,7,8-TCDD peak and 13C-1,2,3,4-TCDD isomers shall be resolved with a valley of $\leq$ 25%, in all calibration standards

$$\text{Valley} = \frac{X}{Y} \times (100)$$

Where:

X=the distinction from the baseline to the bottom of the valley between adjacent peaks.

Y=the peak height of any isomer.

10.3.4.1.In addition, the chromatographic peak separation between 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD in the CC3 solution shall be resolved with a valley of $\leq$ 50%, calculated in a similar fashion as above. The resolution criteria must be evaluated using measurements made on the SICP for the appropriate ions for each isomer. Measurements are not made from total ion current profiles.

10.3.4.2.The relative ion abundance criteria for PCDDs/PCDFs listed in TABLE 5, must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards, in all solutions. The lower and upper limits of the ion abundance ratios represent a $\pm$ 15% window around the theoretical abundance ratio for each pair of selected ions. The ^{37}Cl-2,3,7,8-TCDD cleanup standard contains no ^{35}Cl, thus the ion abundance ratio criterion does not apply to this compound.

10.3.4.3.For all calibrations solutions, the retention times of the isomers must fall within the appropriate retention time windows established by the window defining mix analysis. In addition, the absolute retention times of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard. **For Method 8280A, this section is not applicable.**

10.3.4.4.MS Sensitivity: For all calibration solutions, including the CC1 solution, the signal-to-noise ratio (S/N) must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10 for the internal standard and recovery standard ions.

10.4. Five-Point Initial Calibration

10.4.1. The five calibration solutions outlined in TABLE 4 must be analyzed prior to any sample analyses. The solutions must be analyzed in the following order: CC3, CC1, CC2, CC4, CC5.

10.4.2. Analyze a 2 µL aliquot of each of the five concentration calibration solutions. The identical GC/MS/DS conditions used for the WDM or CPSM solution must also be used for the concentration calibration solutions.

10.4.3. The laboratory must not proceed with the sample analyses until an acceptable initial calibration is determined and documented according to the following criteria:

10.4.3.1.The relative ion abundance criteria listed for PCDDs/PCDFs in TABLE 5, must be met using areas to calculate the ratios.

10.4.3.2. All the analytes must fall within the appropriate retention time windows established by the GC Window Defining Mix. In addition, the absolute retention times of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change by more than 10 seconds between the initial CC3 analysis and the analysis of any other standard. **For Method 8280A, this section is not applicable.**

10.4.3.3.MS Sensitivity: The signal-to-noise (S/N) ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10 for the internal standard and recovery standard ions.

10.5. Relative Response Factors

10.5.1. Calculate the relative response factors (RRFs) for the 17 unlabeled target analytes relative to their appropriate internal standards (RRF_n) according to the formula in Section 10.5.5. For the seven unlabeled analytes and the ^{37}Cl-2,3,7,8-TCDD cleanup standard that are found only in the CC3 solution, only one RRF is calculated for each analyte. For the other 10 unlabeled analytes, calculate the RRF of each analyte in each calibration standard.

10.5.2. Calculate the RRFs for the five labeled internal standards and the cleanup standard relative to the appropriate recovery standard (RRF_{is}) in each calibration standard according to the formula in Section 10.5.5.

10.5.3. There is only one quantitation ion for the ^{37}Cl cleanup standard. Calculate the relative response factor as described for RRF_{is}, using one area for the cleanup standard and the sum of the areas of the ions from the recovery standard.

10.5.4. The RRF_n and the RRF_{is} are dimensionless quantities; therefore, the units used to express the Q_n, Q_{is}, and Q_{rs} must be the same.

NOTE: This protocol is based on the assumption that if the 10 unlabeled 2,3,7,8-substituted isomers provided in the calibration solutions meet linearity criteria, then the seven additional 2,3,7,8-substituted isomers and the cleanup standard in CC3 solution may be assumed to have a sufficiently linear response to be used for quantitation. These eight RRFs cannot be used to determine relative standard deviation, but are used for percent difference determinations and quantitation of target analytes.

10.5.5. Calculations are outlined below:

$$RRF_n = \frac{(A_{n1} + A_{n2}) \times Q_{is}}{(A_{is1} + A_{is2}) \times Q_n}$$

$$RRF_{is} = \frac{(A_{is1} + A_{is2}) \times Q_{rs}}{(A_{rs1} + A_{rs2}) \times Q_{is}}$$

Where:

A_{n1}, A_{n2}	=	integrated areas of the two quantitation ions of the isomer of interest (TABLE 2).
A_{is1}, A_{is2}	=	integrated areas of the two quantitation ions of the appropriate internal standard (TABLE 2)
A_{rs1}, A_{rs2}	=	integrated areas of the two quantitation ions of the appropriate recovery standard (TABLE 2).
RRF_n	=	the response factor of the quantitation ions of the isomer of interest relative to that of the appropriate internal standard.
RRF_{is}	=	the response factor of the internal standard relative to that of the appropriate internal standard

Q_n = quantity of unlabeled PCDD/PCDF analyte injected (ng).

Q_{is} = quantity of appropriate internal standard injected (ng).

Q_{rs} = quantity of appropriate recovery standard injected (ng).

10.5.6. Calculate the relative response factors for the native PCDDs/PCDFs relative to the recovery standards (RRF_{rs}):

Where;

$$RRF_{rs} = RRF_n \times RRF_{is}$$

10.5.6.1. This is used when the sample is diluted to the extent that the MS response of the internal standard is less than 10% of its MS response in the continuing calibration standard (See Section 12.3)

10.5.6.1.1. **For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

10.5.7. Response Factor Criteria

10.5.7.1. Calculate the mean RRF (RRF_{ave}) and percent relative standard deviation (%RSD) of the five RRFs for the unlabeled PCDDs/PCDFs (CC1-CC5) and labeled internal standards present in all five concentration calibration solutions.

10.5.7.2. No mean RRF or %RSD calculations are possible for the 2,3,7,8-substituted isomers or the cleanup standard found only in the CC3 solution.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Mean RRF}} \times 100$$

10.5.7.3. The %RSD of the RRFs for the unlabeled PCDDs/PCDFs (CC1-CC5) and the internal standards must not exceed 15 percent.

10.5.8. If the initial calibration curve requirements are not met, the following suggestions may be useful:

- Check and adjust the GC and/or MS operation conditions,
- Adjust or replace the GC column,
- Adjust the MS for greater or lesser resolution using FC-43. Recalibrate.

10.6. Continuing Calibration (i.e. Daily Standard)

10.6.1. Inject a 2 μL aliquot of the continuing CC3 calibration solution. The continuing calibration solution must be analyzed at the beginning of each 12-hour period to evaluate chromatographic resolution and verify the RRF values used in quantitation.

10.6.2. The identical GC/MS/DS conditions used for the WDM and the initial calibration solutions must also be used for the continuing calibration solution.

10.6.3. GC Column Resolution Criteria. The chromatographic resolution on the DB-5, SP-2331 (or equivalent) columns must meet the QC criteria in Sections 10.3.3 and 10.3.4.

10.6.4. Ion Abundance Criteria. The relative ion abundances listed in TABLE 5 must be met for all PCDD/PCDF peaks, including the labeled internal and recovery standards.

10.6.5. Instrument Sensitivity Criteria. For the CC3 solution, the S/N ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions, and greater than 10.0 for the labeled internal and recovery standards.

10.6.6. Response Factor Criteria. The measured RRFs of each analyte and internal standard in the CC3 solution must be within $\pm$ 30.0% of the mean RRFs established during initial calibration.

$$\% \text{ Difference} = \frac{(RRF_i - RRF_c)}{RRF_i} \times 100$$

Where:

RRF_i=Relative response factor established during initial calibration.

RRF_c=Relative response factor established during continuing calibration.

10.6.7. If any of the criteria listed are not met, the Contractor must take corrective actions and reanalyze the continuing calibration standard (CC3). If the criteria are met after corrective action has been taken, then the sample analysis may proceed.

10.6.8. If the criteria are not met after corrective actions have been taken, then a new initial calibration must be performed, beginning with the analysis of the window defining mix. The new initial calibration must meet all of the QC criteria in Section 10.4 before sample analysis may proceed.

10.7. Instrument Sensitivity Check. In order to demonstrate that the GC/MS/DS system has retained adequate sensitivity during the course of sample analyses, the contractor must analyze the lowest of the standards (CC1) at the end of each 12-hour period during which samples and standards are analyzed.

10.7.1. Analyze a 2 µL aliquot of the CC1 solution, using the identical instrumental conditions used for analysis of samples and standards.

10.7.2. The CC1 solution analyzed at the end of the 12-hour period must meet the following criteria:

- Retention Time Criteria: The absolute retention time of the recovery standards 13C-1,2,3,4-TCDD and 13C-1,2,3,7,8,9-HxCDD shall not change more than 10 seconds between the initial CC3 analysis and then ending CC1 analysis. If the retention times of either of these standards change by more than $\pm$ 10 seconds, the contractor must adjust the switching times of the descriptors and analyze the window defining mix before proceeding with further analyses. **For Method 8280A, this section is not applicable.**

- All the analytes in the CC1 solution must meet the ion abundance ratio criteria in TABLE 5.

- Instrument Sensitivity Criteria: For the CC1 solution, the S/N ratio must be greater than 2.5 for the unlabeled PCDD/PCDF ions and greater than 10.0 for the labeled internal and recovery standards.

10.7.3. If the analysis of the CC1 solution at the end of the 12-hour period fails either the ion abundance or S/N criteria above, the laboratory must take corrective action which may include:

- Performing a new initial calibration, beginning with the analysis if the window defining mix
- Starting a new analytical sequence (See TABLE 9)
- Reanalyzing all samples originally analyzed in the preceding 12-hour time period in which:
  a) No PCDDs/PCDFs were detected
  b) Neither 2,3,7,8-TCDD or 2,3,7,8-TCDF were detected, even if other PCDDs or PCDFs were detected
  c) Any 2,3,7,8-substituted PCDD or PCDF is reported as an Estimated Maximum Possible Concentration
  d) These reanalysis are necessary because poor S/N ratios indicate a loss of sensitivity that could lead to false negative results, underestimation of concentration, or could cause ion abundance ratios to fall outside the QC limits.

For Method 8280A: If the CC1 analysis fails either the ion abundance or S/N criteria, then any samples analyzed during that 12-hour period that indicated the presence of any PCDDs/PCDFs below the method quantitation limit or where EMPC concentrations were reported must be reanalyzed. Samples with positive results above the method quantitation limit need not be reanalyzed.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.1.1. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2. Soxhlet-Dean Stark (SDS) Extraction

11.1.2.1. Do not bake the components of the SDS apparatus as part of routine cleaning. Repeated baking of glassware can cause active sites on the glass surface to absorb PCDDs/PCDFs and other analytes. All glass parts of the SDS apparatus, including the thimbles, must be pre-extracted with toluene for approximately three hours prior to use. Pre-extraction will ensure that the glassware is as clean as possible and minimize cross contamination problems. Discard the used toluene, or pool it for later analysis to verify the cleanliness of the glassware.

11.1.2.2. The extraction of soil/sediment, fly ash, and particulates from water samples will require the use of a Soxhlet thimble. Prior to pre-extraction, prepare the thimble by adding 5g of 70/230 mesh silica gel to the thimble to produce a thin layer in the bottom of the thimble. This layer will trap fine particles in the thimble. Add 15-20g of quartz sand on top of the silica gel and place the thimble in the extractor.

11.1.2.3. After pre-extraction for three hours, allow the apparatus to cool and remove the thimble. Mix the appropriate weight of sample with the sand in the thimble, being careful not to disturb the silica gel layer.

11.1.2.3.1. If the sample aliquot to be extracted contains large lumps or is otherwise not easily mixed in the thimble, the sand and sample may be mixed in another container. Transfer approximately 2/3 of the sand from the thimble to a clean container, being careful not to disturb the silica gel, and the sample and a clean spatula, and transfer the sand/sample mixture to the thimble.

11.1.2.3.2. If a sample with particularly high moisture content is to be extracted, it may be helpful to leave a small conical depression in the material in the thimble. This procedure will allow the water to drain through the thimble more quickly during the early hours of the extraction. As the moisture is removed during the first few hours of extraction, the depression will collapse, and the sample can be uniformly extracted.

11.2. Chemical Waste Sample Extraction

11.2.1. Assemble a flask (125 mL), a Dean Stark trap, and a condenser, and pre-extract with toluene for three hours. Pre-extraction will ensure that the glassware is as clean as possible and minimize cross-contamination problems. Discard the used toluene, or pool it for later analysis to verify cleanliness of the glassware.

11.2.2. Oily Sludge/Wet Fuel Oil: Weigh about 1g of sample to two decimal place into a tarred pre-extracted 125 mL flask. Add internal standard solution (TABLE 8) to the sample in the flask. Attach the pre-extracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours

11.2.2.1. Continue refluxing the sample until all the water has been removed. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 11.2.7.

11.2.2.2. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.2.2.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.3. Stillbottom/Oil: Weigh about 1g of sample to two decimal places into a tarred pre-extracted 125 mL flask. Add internal standard solution (See TABLE 8) to the sample in the flask. Attach the pre-extracted Dean Stark water separator and condenser to the flask, and extract the sample by refluxing it with 50 mL of toluene for at least three hours.

11.2.3.1. Cool the sample, and filter the toluene extract through a rinsed glass fiber filter into a 100 mL round bottom flask. Rinse the filter with 10 mL of toluene, and combine the extract and rinsate. Concentrate the combined solution to approximately 10 mL using a rotary evaporator as described in Section 11.2.7.

11.2.3.2. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.3.2.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.4. Fly Ash Sample Extraction

11.2.4.1. Weigh about 10g of the fly ash to two decimal places and transfer to an extraction jar. Add internal standard solution (See TABLE 8) to the sample.

11.2.4.2. Add 150 mL of 1N HCl to the fly ash sample in the jar. Seal the jar with the Teflon-lined screw cap, place on a mechanical shaker, and shake for three hours at room temperature..

11.2.4.3. Rinse a Whatman #1 (or equivalent) filter paper with toluene, and then filter the sample through the filter paper in a Buchner funnel into a 1L receiving flask. Wash the fly ash with approximately 500 mL distilled water.

11.2.4.4. Mix the fly ash with the sand in a pre-extracted thimble and place the filter paper on top of the sand. Place the thimble in a SDS extractor, add 200 mL toluene, and extract for 16 hours.

11.2.4.4.1. The solvent must cycle completely through the system 5-10 times per hour. Cool and filter the toluene extract through a rinsed glass fiber filter into a 500 mL round bottom flask. Rinse the filter with 10 mL of toluene. Concentrate the extract as described in Section 11.2.7.

NOTE: *A blank must be analyzed using a piece of filter paper handled in the same manner as the fly ash sample.*

11.2.4.5. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.4.5.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.5. Soil/Sediment Sample Extraction

11.2.5.1. An extremely wet sample may required centrifugation to remove standing water before extraction.

11.2.5.2. Weigh about 10g of soil to two decimal places and transfer to a pre-extracted thimble (See Section 11.1.2). Mix the sample with the quartz sand and add internal standard solution (see TABLE 8) to the sample/sand mixture. Add small portions of the solution at several sites on the surface of the sample/sand mixture.

11.2.5.3.Place the thimble in the SDS apparatus. Add 200-250 mL toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 times per hour.

11.2.5.4.Estimate the percent solids content of the soil/sediment sample by measuring the volume of water evolved during the SDS extraction procedure. For extremely wet samples, the Dean Stark trap may need to be drained one or more times during the 16-hour extraction. Collect the water from the trap and measure its volume to the nearest 0.1 mL. Assume a density of 1.0 g/mL and calculate the percent solids content according to the following formula:

$$\text{Percent Solids} = \frac{(\text{Wet weight of sample} - \text{Weight of water})}{\text{Wet weight of sample}} \times 100$$

11.2.5.5.Concentrate this extract as described in Section 11.2.7.

11.2.5.6.Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.5.6.1.**For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.6. Water Sample Extraction

11.2.6.1.Allow the sample to reach ambient temperature. Add 1 mL of the acetone-diluted internal standard solution (See TABLE 8) to the sample bottle. Cap the bottle and mix the sample by gently shaking for 30 seconds. Filter the sample through a glass fiber filter that has been rinsed with toluene.

***NOTE:** Reagent water used as a blank must also be filtered in a similar fashion and subjected to the same cleanup analysis as the water samples.*

11.2.6.1.1.If the total dissolved and suspended solids contents are too much to filter through the glass fiber filter, centrifuge the sample, decant, and then filter the aqueous phase. Combine the solids from the centrifuge bottle(s), the particulate on the filter, and the filter itself and proceed with the SDS extraction in Section 11.2.6.2.

11.2.6.1.2. The filtered aqueous sample is poured into a 2 L separatory funnel. Add 100 mL methylene chloride to the sample bottle, seal, and shake for 60 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst shall employ mechanical techniques to complete the phase separation (i.e. glass stirring rod). Drain the methylene chloride extract into a 500 mL round bottom flask by passing the extract through a funnel packed with a glass wool plug and half-filled with anhydrous sodium sulfate. Extract the water sample two more times using 100 mL of fresh methylene chloride each time. Drain each extract through the funnel into round bottom flask. After the third extraction, rinse the sodium sulfate with at least 30 mL of fresh methylene chloride. Concentrate this extract as described in Section 11.2.7.

11.2.6.2. Combine the filtered particulate portion of the sample with the quartz sand in the extraction thimble. Add the filter on top of the particulate/sand mixture and place the thimble into a pre-extracted SDS apparatus.

11.2.6.2.1. Add 200-250 mL of toluene to the SDS apparatus and reflux for 16 hours. The solvent must cycle completely through the system 5-10 time per hour. Concentrate this extract as described in Section 11.2.7.

11.2.6.3. Determine the original sample volume by weighing the empty sample container and assume the specific gravity of the sample to be 1.0 g/mL. Record the sample volume.

11.2.6.4. Prepare a sample aliquot for the duplicate sample analysis and a sample aliquot for the spiked sample analysis.

11.2.6.4.1. **For Method 8280A:** Prepare sample aliquots for the matrix spike/matrix spike duplicate analysis.

11.2.7. Macro-Concentration Procedures (All Matrices)

11.2.7.1. Prior to cleanup, extracts from all matrices must be concentrated to approximately 2 mL (near dryness). In addition, the concentrated extracts from the aqueous filtrate and the filtered particulates must be combined prior to cleanup. Prior to concentrating all extracts add 200 µL of tetradecane.

11.2.7.2. Concentration by Rotary Evaporator

11.2.7.2.1. According to manufacturer's instructions, assemble the rotary evaporator and warm the water bath to 65°C. Between samples, rinse 2-3 mL aliquots of toluene down the feed tube into a waste beaker.

11.2.7.2.2. Attach the round bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system and begin rotating the sample flask.

11.2.7.2.3. Lower the flask into the water bath and adjust the speed of rotation and the temperature as required to complete the concentration in 15-20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask should be steady and no bumping or visible boiling of the extract shall occur.

NOTE: *If the rate of concentration is too fast, analyte loss may occur.*

11.2.7.2.4. When the liquid in the concentration flask has reached an apparent volume of 2 mL, remove the flask from the water bath, and stop the rotation. Slowly and carefully emit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Detach the flask from the rotary evaporator. Rinse the feed tube with approximately 2 mL of toluene and hexane prior to attaching the next extract.

11.2.7.3. Extracts of Chemical Waste, Fly Ash, and Soil/Sediment Samples

11.2.7.3.1. For chemical waste, fly ash, and soil/sediment samples, the extract must be concentrated to approximately 2 mL prior to acid-base washing treatment. Concentrate the extract as described above.

11.2.7.3.2. Transfer the concentrated extract to a 500 mL separatory funnel. Rinse the flask with toluene and add the rinse to the separatory funnel. Proceed with acid-base washing treatment per Section 11.2.8.

11.2.7.4. Extracts of Aqueous Filtrates

11.2.7.4.1. Extracts of the aqueous filtrate of water samples are in methylene chloride which are concentrated to approximately 2 mL by rotary evaporator prior to combining with the toluene extract of the particulates.

11.2.7.4.2. Combine the extract of the filtrate with the extract of the particulates as described in Section 11.2.7.5.

11.2.7.5. Extracts of Particulates from Aqueous Samples

11.2.7.5.1. If the extract is from the particulates from an aqueous sample, it must be concentrated to approximately 2 mL by rotary evaporator, and combined with concentrated extract of the filtrate (Section 11.2.7.4) prior to acid-base washing treatment.

11.2.7.5.2. Concentrate the combined extract to approximately 2 mL (the volume of the toluene) by rotary evaporator.

11.2.7.5.3. Transfer the concentrated combined extract to a 500 mL separatory funnel. Rinse the concentrator with three 5 mL volumes of hexane and add each rinse to the separatory funnel. Proceed with acid-base washing treatment according to Section 11.2.8.

11.3. There are several useful methods to decrease or eliminate emulsion in aqueous samples when extracting with DCM. These methods may include stirring with a pipet to manually breakup the emulsions or to transfer the sample into centrifuge tubes and centrifuge at approximately 3000 RPM. The most useful method is to use a 1:1 NaOH/H2O solution to change the pH enough to disrupt the emulsion phase, which works 90% of the time. The following procedure describes how to prepare and use the solution to decrease or eliminate emulsions in aqueous samples during the liquid/liquid extraction step.

11.3.1. Preparing the solution:

Add 1.0L of reagent grade NaOH solution to an empty 2.0L NaOH container. Then add 1.0L of DI H2O to the container and leave the container in secondary containment with the lid off. ***(The solution will begin to heat so let the solution stand equilibrium is met and the solution is at room temperature).*** When this process is complete, the solution will then be ready for use in the samples.

11.3.2 Using the solution to decrease emulsions:

11.3.2.1 Check the pH of the sample to make sure pH is between 3 and 7. If pH is greater than 7, then consult supervisor and client for instructions. Pour approximately 100 mL of 1:1 NaOH/H20 into a 1.0L AGB.

11.3.2.2 Drain the sample with emulsion from the 2.0L separatory funnel into the 1:1 NaOH/H2O and let stand. Empty aqueous waste into the LLE waste drum.

11.3.2.3 Pour the solution with DCM back into the same 2.0L separatory funnel and drain the DCM phase through Na2SO4 into a 500mL roundbottom. Empty the aqueous waste into the LLE waste drum.

11.4. Extract Cleanup Procedures (All Matrices)

11.4.1.1. Prior to cleanup, all extracts are spiked with the ^{37}Cl-2, 3,7,8-TCDD cleanup standard. The recovery of this standard is used to monitor the efficiency of the cleanup procedures. Spike 50 µL of the cleanup standard (or a larger volume of diluted solution containing 25 ng of ^{37}Cl-2,3,7,8-TCDD) into each separatory funnel containing an extract, resulting in a concentration of 0.25 ng/µL in the final extract analyzed by GC/MS. Add 150 mL of hexane to dilute the extract in the separatory funnel.

11.4.1.1.1. **For Method 8280A:** The procedures outlined in Sections 11.2.8.2 through 11.2.8.5 need not apply to uncolored extracts, but all the other cleanup procedures should be employed, regardless of the color of the extract.

11.4.1.2. Partition the concentrated extract against 40 mL of concentrated sulfuric acid. Shake for thirty seconds. Remove and discard the acid layer (bottom). Repeat the acid washing until there is no visible color in the acid layer. (Perform acid washings a maximum of four times).

CAUTION: *Concentrated sulfuric acid is hazardous and should be handled with care. A faceshield shall be used when handling bulk acids and bases.*

11.4.1.3. Partition the concentrated extract against 40 mL of distilled water. Shake for thirty seconds. Remove and discard the aqueous layer (bottom).

11.4.1.4. Partition the concentrated extract against 40 mL of 10N NaOH. Shake for thirty seconds. Remove and discard the base layer (bottom). Repeat the base washes until there is no color visible in the bottom layer (perform base washes a maximum of four times). Strong base, NaOH, is known to degrade certain PCDDs/PCDFs; therefore, contact time should be minimized.

11.4.1.5. Partition the concentrated extract against 40 mL of distilled water. Shake for thirty seconds. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring it through a funnel containing anhydrous sodium sulfate. Collect the extract in an appropriate size round bottom flask. Wash the separatory funnel with two 15 mL portions of hexane, pour through the funnel and combine the extracts. Concentrate the extracts to 1.0 mL using the procedures described in Section 11.2.7.

11.4.2. Silica Gel and Alumina Column Chromatographic Procedure

11.4.2.1. Column 1: Insert a glass wool plug onto the bottom of a 20 mm disposable glass column. Add 1g silica gel and tap the column gently to settle the silica gel. Add 2g sodium hydroxide-impregnated silica gel, 1g silica gel, 4g sulfuric acid-impregnated silica gel, and 2g silica gel. Top with 1g anhydrous sodium sulfate. Tap the column gently after each addition. A small positive pressure (5 psi) of clean nitrogen may be used if needed.

11.4.2.2. Column 2: Insert a glass wool plug onto the bottom of a 16 mm disposable glass column. Add 6g of the activated acid alumina. Top with 1g anhydrous sodium sulfate. Tap the top of the column gently.

11.4.2.2.1. Check each new batch of silica gel and alumina and maintain the results of the analyses on file. To accomplish this, combine 100 µL of the internal standard solution and 50 µL of matrix spike solution with 850 µL of hexane. Process this solution through both columns in the same manner as a sample extract (Section 11.2.10.3). Concentrate the continuing calibration solution to a final volume of 50 µL. Proceed to analysis (Section 11.3). If the recovery of any of the analytes is less than 80%, this batch of carbon/silica mixture may not be used.

11.4.2.3. Add 20 mL of hexane to each column until the packing is free of air bubbles. A small positive pressure (5 psi) of clean dry nitrogen may be used if needed. Check the columns for nitrogen may be used if needed. Check the columns for channeling. If channeling is present, discard the column.

CAUTION: Do not tap a wetted column.

11.4.2.4. Assemble the two columns such that the eluate from Column 1 (silica gel) drains directly into Column 2 (alumina).

11.4.2.5. Transfer the extract from Section 11.2.8. to the top of the silica gel column. Rinse the flask with enough hexane (1-2 mL) to complete the quantitative transfer of the sample to the surface of the silica.

11.4.2.6. Using 90 mL of hexane, elute the extract from Column 1 directly onto Column 2, which contains the alumina.

***CAUTION:** Do not allow the alumina column to run dry.*

11.4.2.7. Add 20 mL of 20% methylene chloride/80% hexane (v/v) to Column 2, and elute until the solvent level is just below the top of the alumina.

11.4.2.8. Add 26 mL of 80% methylene chloride/20% hexane (v/v) to Column 2, and collect the eluate in a culture tube.

11.4.2.9. Add 200 µL of tetradecane and concentrate the extract to near dryness using a turbo-evaporator apparatus. The extract is now ready to be transferred to the carbon column.

11.4.3. Carbon Column Chromatographic Procedure

11.4.3.1. Thoroughly mix 95g activated silica gel and 5.0g charcoal. Activate the mixture at 190°C for twelve hours and store in a charcoal/silica oven at 190°C.

11.4.3.1.1. Check each new batch of the charcoal/silica and maintain the results from the analyses for examination. To accomplish this, add 100 µL of the internal standard solution and 50 µL of matrix spike solution to 850 µL of hexane. Process the spiked solution in the same manner as a sample extract (Section 11.2.11.1.2 through 11.2.11.5). Concentrate the solution to 50 µL and proceed with Section 11.3. If the recovery of any of the analytes is less than 80%, this batch of carbon/silica mixture may not be used.

11.4.3.2. Prepare an 8-inch glass column by cutting off each end of a 5 mL disposable serological pipet. Insert a glass wool plug at one end of the column and pack it with 0.30 g of the charcoal/silica mixture. Insert an additional glass wool plug in the other end. See Figure 2.

CAUTION: *It is very important that the column be packed properly to ensure that carbon fines are not carried into the eluate. PCDDs/PCDFs will adhere to the carbon fines and greatly reduce recovery. If carbon fines are carried into the eluate in Section 11.2.10.5, filter the eluate using a 0.45 micron filter (pre-rinsed with toluene), then proceed to Section 11.3.*

11.4.3.3. Pre-rinse with 5 mL hexane in both directions.

11.4.3.3.1. Pre-elute 2 mL of toluene in Direction B 2.

11.4.3.3.2.mL 75:20 methylene chloride:methanol.

11.4.3.3.3.mL 1:1 Cyclohexane: methylene chloride .

11.4.3.3.4.mL Hexane

11.4.3.3.5.Discard all the column rinsates.

11.4.3.4.While the column is still wet, transfer the concentrated eluate from Section 11.2.9.9. to the prepared carbon column. Rinse the eluate container with two 1.0 mL portions of hexane and transfer the rinses to the carbon column. Elute the column with the following sequence of solvents:

11.4.3.4.1.mL of Cyclohexane/Methylene Chloride (50:50 v/v).

11.4.3.4.2.mL of Methylene Chloride/Methanol (75:20 v/v)

NOTE: *The above two eluates may be collected, combined and used as a check on column efficiency.*

11.4.3.5.Once the solvents have eluted through the column, turn the column over, elute the PCDD/PCDF fraction with 15 mL of toluene, and collect the eluate.

11.4.4. Final Concentration

11.4.4.1.Evaporate the toluene fraction from Section 11.2.10.5 to approximately 1.0 mL with N_2 via turbo-evaporator.

11.4.4.2.Transfer the extract to a 2.0 mL conical vial using a hexane rinse.

CAUTION: *Do not evaporate the sample extract to dryness.*

11.4.4.3.Add 100 µL tetradecane to the extract and reduce the volume to 100 µL using a gentle stream of clean dry nitrogen. The final extract volume should be 100 µL of tetradecane. Seal the vial and store the sample extract in the dark at ambient temperature until prior to GC/MS analysis.

11.4.4.4.Transfer a 50 µL aliquot of the extract to a 0.3 mL vial and add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL in a 50 µL volume. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.

11.5. GC/MS Analysis

11.5.1. Inject a 2 µL aliquot of the extract into the GC/MS instrument. Reseal the vial containing the original concentrated extract.

11.5.2. Analyze the extract by GC/MS and monitor all of the ions listed in TABLE 2. The same MS parameters used to analyze the calibration solutions shall be used for the sample extracts.

11.6. Dilutions

11.6.1. If the concentration in the final extract of any analyte exceeds the upper method calibration limit (MCL) for that compound, the linear range of response versus concentration may have been exceeded. In such cases, the following corrective actions will be undertaken:

- If the signal for the analyte has saturated the detector, a single dilution and reanalysis of the extract will be made in an attempt to bring the signal within the range of the detector. The reported concentration for the analyte will be qualified appropriately.

- If the signal for the analyte is above the MCL, but does not saturate the detector, the concentration will be reported and qualified as "E."

- With the approval of the client, samples may be reextracted and/or reanalyzed with the following adjustments in order to provide a concentration that meets client-specific data quality objectives.

- Extract and analyze one tenth of the original aliquot. This option is appropriate only if it will provide analyte concentration within the MCL and if the sample aliquot will be representative.

- Extract an aliquot large enough to be representative, and increase the concentration of internal standard and surrogate spike components added prior to the extraction. The extract is then diluted either prior to or after the clean up procedures.

- Dilute the original extract. Internal standard components are respiked at an appropriate level prior to analysis. In this case, the internal standard recoveries are taken from the original analysis.

11.6.1.1. **For Method 8280A:** A dilution is only necessary if the detector has been saturated.

11.6.2. An appropriate dilution will result in the largest peak in the diluted sample falling between the mid-point and high-point of the calibration range.

11.6.3. Dilutions are performed using an aliquot of the original extract of which approximately 50 µL remains. Remove an appropriately sized aliquot from the vial and add it to a sufficient volume of tetradecane in a clean 0.3 mL conical vial. Add sufficient recovery standard solution to yield a concentration of 0.5 ng/µL. Reduce the volume of the extract back down to 50 µL using a gentle stream of dry nitrogen.

11.6.4. The dilution factor is defined as the total volume of sample aliquot and clean solvent (50 µL) divided by the volume of the sample aliquot that was diluted.

11.6.5. Inject 2 µL of the diluted sample extract into the GC/MS and analyze according to Section 11.3.

11.6.6. Diluted samples in which the MS response of any internal standard is < 10% of the MS response of that internal standard in the most recent continuing calibration standards are quantified using the recovery standards.

11.6.6.1. **For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

11.7. Identification Criteria

11.7.1. For a gas chromatographic peak to be unambiguously identified as a PCDD or PCDF, it must meet all of the following criteria:

11.7.1.1. Retention Times

11.7.1.1.1. Retention times are required for all chromatograms; scan numbers are optional. Retention times shall either be printed at the apex of each peak on the chromatogram, or each peak shall be unambiguously labeled with an identifier that refers to the quantitation report, or combination of both shall contain the retention time of each peak and its area.

11.7.1.1.2. In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time (RT) at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

11.7.1.1.3. In order to make a positive identification of the 2,3,7,8-substituted isomers for which a labeled standard is not available, the relative retention time (RRT) of the analyte must be within 0.05 RRT units of the RRT established by the continuing calibration. The RRT is calculated as follows:

$$RRT = \frac{\text{Retention Time of Analyte}}{\text{Retention Time of Corresponding Internal Standard}}$$

11.7.1.1.4. For non-2,3,7,8-substituted compounds (tetra through hepta), the retention time must be within the retention time windows established by the window defining mix for the corresponding homologue (See Section 10.2).

11.7.1.1.5. In order to assure that retention time shifts do not adversely affect the identification of PCDDs/PCDFs, the absolute retention times of the two recovery standards added to every sample extract prior to analysis, may not shift by more than $\pm$ 10 seconds from their retention times in the continuing calibration standard. **For Method 8280A, this section is not applicable.**

11.7.2. Peak Identification

11.7.2.1. All of the specified ions listed in TABLE 2 for each PCDD/PCDF homologue and labeled standards must be present in the SICP. The ion current response for the two quantitation ions and the M- $[COCl]^+$ ions for the analytes must maximize simultaneously ($\pm$ 2 seconds). This requirement also applies to the internal standards and recovery standards. For the cleanup standard, only one ion is monitored.

11.7.3. Signal-To-Noise Ratio

11.7.3.1. The integrated ion current for each analyte ion listed in TABLE 2 must be at least 2.5 times background noise and must not have saturated the detector. The internal standard ions must be at least 10.0 times background noise and must not have saturated the detector. However, if the M-$[COCl]^+$ ion does not meet the 2.5 times S/N requirement but meets all other criteria listed in Section 11.5 and, in the judgment of the GC/MS Interpretation Specialist, the peak is a PCDD/PCDF, the peak may be reported as positive.

11.7.4. Ion Abundance Ratios

11.7.4.1. The relative ion abundance criteria listed in TABLE 5 for native analytes and internal standards must be met using peak areas to calculate ratios.

11.7.4.2. If interferences are present and ion abundance ratios are not met using peak areas, but all other qualitative identification criteria <u>are</u> met (RT, S/N, presence of all three ions), the chemist may use peak heights to evaluate the ion ratio.

11.7.4.3. If, in the judgment of the analyst, the peak is a PCDD/PCDF, then report the ion abundance ratios determined using peak heights. <u>Quantitate</u> the peaks using peak heights rather than areas for both the target analyte and the internal standard.

11.7.4.4. The identification of a GC peak as a PCDF cannot be made if a signal having S/N greater than 2.5 is detected at the same retention time ($\pm$ 2 seconds) in the corresponding PCDPE channel (See TABLE 2). If a PCDPE is detected, an EMPC should be calculated for this GC peak regardless of the ion abundance ratio.

12. DATA ANALYSIS AND CALCULATIONS

12.1. For GC peaks that have met all the identification criteria outlined in Section 11.5, calculate the concentration of the individual PCDD or PCDF isomers using the following formula:

12.1.1. All matrices other than water:

$$\text{Conc. } (\mu g/kg) = \frac{Q_{is} \times (A_{n1} + A_{n2})}{W \times (A_{is1} + A_{is2}) \times RRF_n}$$

12.1.2. Water matrices:

$$\text{Conc. } (ng/L) = \frac{Q_{is} \times (A_{n1} + A_{n2})}{V \times (A_{is1} + A_{is2}) \times RRF_n}$$

Where:

A_{n1}, A_{n2} =integrated ion abundances (peak area) of the quantitation ions of the isomer of interest (TABLE 2).

A_{is1}, A_{is2} =integrated ion abundances (peak areas) of the quantitation ions of the appropriate internal standard (TABLE 2).

***NOTE:** In instances where peak heights are used to evaluate ion abundance ratios due to interference (see Section 11.5.4), substitute peak heights for areas in the formula above.*

W =weight of sample extracted, in grams.

V =volume of sample extracted, in liters.

Q_{is}

= quantity of the appropriate internal standard added to the sample prior to extraction, ng.

RRF_n=calculated relative response factor from continuing calibration (See Section 10.6).

12.1.3. For solid matrices, the units of ng/g that result from the formula above are equivalent to µg/Kg. Using isotope dilution techniques for quantitation, the concentration data are recovery corrected, and therefore, the volume of the final extract and the injection volume are implicit in the value of Qis.

12.1.3.1.For homologues that contain only one 2,3,7,8-substituted isomer (TCDD, PeCDD, HpCDD, OCDD, TCDF, and OCDF), the RRF of the 2,3,7,8-

substituted isomer from the continuing calibration (See Section 10.6) will be used to quantitate both the 2,3,7,8-substituted isomers and the non-2,3,7,8-substituted isomers.

12.1.3.2. For homologues that contain more than one 2,3,7,8-substituted isomer (HxCDD, PeCDF, HxCDF, and HpCDF), the RRF used to calculate the concentration of each 2,3,7,8-substituted isomers will be the RRF determined for that isomer during the continuing calibration (See Section 10.6)

12.1.3.3. For homologues that contain one or more non-2,3,7,8-substituted isomers, the RRF used to calculate the concentration of these isomers will be the lowest of the RRFs determined during the continuing calibration (See Section 10.6) for the 2,3,7,8-substituted isomers in that homologue. This RRF will yield the highest possible concentration for the non-2,3,7,8-substituted isomers.

NOTE: *The relative response factors of given isomers within any homologue may be different. However, for the purpose of these calculations, it will be assumed that every non-2,3,7,8-substituted isomer for a given homologue will have the same relative response factor. In order to minimize the effect of this assumption on risk assessment, the 2,3,7,8-substituted isomer with the lowest RRF was chosen as representative of each homologue. All relative response factor calculations for the non-2,3,7,8-substituted isomers in a given homologue are based on that isomer.*

12.2. In addition to the concentrations of specific isomers, the total homologue concentrations are also reported. Calculate the total concentration of each homologue of PCDDs/PCDFs as follows:

Total Concentration = sum of the concentrations of every positively identified isomer of each PCDD/PCDF homologue.

12.2.1. The total must include the non-2,3,7,8-substituted isomers as well as the 2,3,7,8-substituted isomers that are also reported separately.

12.3. If the area of any internal standard in a diluted sample is less than 10% of the area of that internal standard in the continuing calibration standard, then the unlabeled PCDD/PCDF concentrations in the sample shall be estimated using the formula below. The purpose is to ensure that there is an adequate MS response for quantitation in a diluted sample. A smaller aliquot of the sample may require smaller dilutions and therefore yield a larger area for the internal standard in the homogeneity of the sample and the representativeness of the aliquot take for extraction.

12.3.1. All matrices other than water:

$$\text{Conc. } (\mu g/Kg) = \frac{Q_{rs} \times (A_{n1} + A_{n2}) \times D}{W \times (A_{rs1} + A_{rs2}) \times RRF_{rs}}$$

12.3.2. Water matrices:

$$\text{Conc. } (ng/L) = \frac{Q_{rs} \times (A_{n1} + A_{n2}) \times D}{V \times (A_{rs1} + A_{rs2}) \times RRF_{rs}}$$

D = Dilution factor (See Section 11.4).

(See Section 10.5.5 and 12.1 for identification of the rest of the terms.)

12.3.2.1. **For Method 8280A:** The RRF_{rs} method of quantitation is only used when the sample is diluted to the extent that the S/N ratio for the internal standard is less than 10.0.

12.4. Report results for soil/sediment, fly ash, and chemical waste samples in micrograms per kilograms (µg/Kg) or nanograms per gram (ng/g) and water samples in nanograms per liter (ng/L).

12.5. Calculate the percent recovery for each internal standard and the cleanup standard in the sample extract, R_{is}, using the following formula:

$$R_{is} = \frac{(A_{is1} + A_{is2}) \times Q_{rs}}{(A_{rs1} + A_{rs2}) \times RRF_{is} \times Q_{is}} \times 100\%$$

(See Section 10.5.5 and 12.1 for identification of the terms.)

NOTE: *When calculating the recovery of the ^{37}Cl-2,3,7,8-TCDD cleanup standard, only one m/z is monitored for this standard; therefore only one peak will be used in the numerator of this formula. Use* ***both*** *peak areas if the 13C-1,2,3,4-TCDD recovery standard in the denominator.*

12.6. Sample Specific Estimated Detection Limit

12.6.1. The sample specific Estimated Detection Limit (EDL) is the estimate made by the laboratory of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The estimate is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc.

12.6.2. An EDL is calculated for each 2,3,7,8-substituted isomer that is not identified, regardless of whether or not non-2,3,7,8-substituted isomers in that homologue are present. The EDL is also calculated for 2,3,7,8-substituted isomers giving responses for both the quantitation ions that are less than 2.5 times the background level.

12.6.3. Using the formula below to calculate an EDL for each absent 2,3,7,8-substituted PCDD/PCDF. The background level (H_x) is determined by measuring the height of the noise at the expected retention times of both quantitation ions of the particular 2,3,7,8-substituted isomer. The expected retention time is determined from the most recent analysis of the CC3 standard on the same GC/MS system.

12.6.3.1. All matrices other than water:

$$\text{EDL } (\mu g/kg) = \frac{2.5 \text{ x } Q_{is} \text{ X } (H_{x1} + H_{x2}) \text{ x } D}{W \text{ x } (H_{is1} + H_{is2}) \text{ x } RRF_n}$$

12.6.3.2. Water matrices:

$$\text{EDL } (ng/L) = \frac{2.5 \text{ x } Q_{is} \text{ x } (H_{x1} + H_{x2}) \text{ x } D}{V \text{ x } (H_{is1} + H_{is2}) \text{ x } RRF_n}$$

Where:

H_{x1},H_{x2} =Peak heights of the noise for both of the quantitation ions of the 2,3,7,8-substituted isomer of interest.

H_{is1},H_{is2} =Peak heights of both the quantitation ions of the appropriate internal standards.

D =Dilution factor (See Section 11.4).
(See Section 12.1 for Q_{is}, RRF_n, W, and V)

***NOTE:** If the congener class is non-detect, the largest relative response factor (RRF) for that class will be used to calculate the congener's estimated detection limit.*

12.7. Estimated Maximum Possible Concentration (EMPC)

12.7.1. An estimated maximum possible concentration is calculated for 2,3,7,8-substituted isomers that are characterized by the response with a S/N of at least 2.5 for both the quantitation ions, but that do not meet all the identification criteria in Section 11.5.

12.7.2. Calculate the EMPC according to the following formula:

12.7.2.1. All matrices other than water:

$$\text{EMPC } (\mu g/L) = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF_n \times W}$$

12.7.2.2. Water:

$$\text{EMPC}(ng/L) = \frac{(A_{x1} + A_{x2}) \times Q_{is} \times D}{(A_{is1} + A_{is2}) \times RRF \times V}$$

Where:

A_{x1}, A_{x2} = areas of both quantitation ions. (See Section 10.5.5 and 12.1 for identification of the rest of the terms.)

12.8. Toxicity Equivalency Factor (TEF) Calculation

12.8.1. The 2,3,7,8-TCDD toxicity equivalence of PCDDs/PCDFs present in the sample is calculated according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Centers for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor to each of the seventeen 2,3,7,8-substituted PCDDs/PCDFs shown in TABLE 1. The 2,3,7,8-TCDD toxicity equivalence of the PCDDs/PCDFs present in the sample are calculated by summing the product of the TEF and the concentration for each of the compounds listed in TABLE 1.

12.8.2. The exclusion of homologues such as mono-, di-, tri-, and the non-2,3,7,8-substituted isomers in the higher homologues does not mean that they are not toxic. Their toxicity, as estimated at this time, is much less that the toxicity of the compounds listed in TABLE 1. Hence, only 2,3,7,8-substituted isomers are included in the TEF calculations. The procedure for calculating the 2,3,7,8-TCDD toxic equivalence cited above is not claimed by the CDWG to be based on a thoroughly established scientific foundation. Rather, the procedure represents a "Consensus Recommendation on Science Policy."

12.8.3. When calculating the 2,3,7,8-TCDD toxicity equivalence of a sample, include only those 2,3,7,8-substituted isomers that were detected in the sample and met all of the qualitative identification criteria in Section 11.5. Do not include EMPC or EDL values in the TEF calculations.

12.8.4. The 2,3,7,8-TCDD toxicity equivalence of a sample is used to determine when second column confirmation may be required.

12.9. Due to a variety of situations that may occur during method performance, the laboratory is required to reextract and reanalyze certain samples or groups of samples. Except in the case of dilutions, the term "rerun" shall indicate sample extraction, cleanup, and reanalysis. When dilutions are required, the original extract shall be diluted and reanalyzed.

12.9.1. When the rerun is required due to matrix effects, interferences, or other problems encountered, the client, upon authorization to perform, will pay the laboratory for the reruns. When the rerun is required due to laboratory materials, equipment or instrumentation problems, or lack of laboratory adherence to specified method procedures, then the rerun shall not be billable.

12.9.2. The following sample reruns may be required as defined below:

12.9.2.1.If the original sample has a percent recovery of any internal standard or the cleanup standard outside of the range of 25-150%, then reextraction and reanalysis is required, upon client approval

12.9.2.2.If the internal standards are not present with at least a 10/1 S/N ratio at their respective m/zs (316, 318, 332, 334, 402, 404, 420, 422, 470, and 472), the reextraction and reanalysis are required. If the ^{37}Cl-2,3,7,8-TCDD is not present with at least a 10/1 S/N ratio at m/z 328, then reextraction and reanalysis may be required.

12.9.2.3. If any of the internal standard ion abundance ratios as specified in TABLE 5 are outside the method specified control limits, the laboratory must reanalyze the sample extract on a second GC column with different elution characteristics. No reextraction is required for such an analysis. **For Method 8280A, this section is not applicable.**

12.9.2.4. If the absolute retention time of either the 13C-1,2,3,4-TCDD or 13C-1,2,3,7,8,9-HxCDD recovery standard in a sample extract shifts by greater than 10 seconds from the retention time of that standard in the continuing calibration standard, then the sample extract must be reanalyzed after the laboratory has investigated the cause of the retention time shift and taken corrective action. No reextraction is required for such an analysis. **For Method 8280A, this section is not applicable.**

12.9.3. If the calculated concentration of the unlabeled PCDDs/PCDFs exceeded the initial calibration range, the sample shall be diluted and reanalyzed. See Section 11.4 for specific corrective actions.

12.9.4. The following sample reruns shall be performed at the laboratory's expense and shall not be billable under the terms of the contract:

12.9.4.1. All positive samples associated with a contaminated method blank and any samples which contain peaks that do not meet all of the qualitative identification criteria in Section 11.5 associated with a contaminated method blank must be reextracted and reanalyzed. Acceptable laboratory method blanks must not contain any chemical interference or electronic noise at the m/z of the specified unlabeled PCDD/PCDF ions that is greater than five percent of the signal of the appropriate internal standard quantitation ion. A peak that meets identification criteria in the method blank must not exceed two percent of the signal of the appropriate internal standard. **For Method 8280A, this section is not applicable.**

12.9.4.2. If the chromatographic peak separation between 13C-2,3,7,8-TCDD and 13C-1,2,3,4-TCDD is not resolved with a valley of $\leq$ 25% on the DB-5 (or equivalent) column, or 2,3,7,8-TCDD is not resolved from the closest eluting isomer with a valley of $\leq$ 25% on the SP-2331 (or equivalent) column, then the laboratory shall adjust the GC/MS operating conditions and rerun the affected sample. This criterion applies to sample analyses. If this criterion is not met for a calibration standard, all associated samples must be rerun. **There is no TCDD resolution criteria for method 8280A.**

13. METHOD PERFORMANCE

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required expertise.

14. POLLUTION PREVENTION

14.1. No solvents of any kind or in any amount are to be disposed of in the sinks or evaporated in the hoods.

15. WASTE MANAGEMENT

15.1. Waste management in the procedure must be segregated and disposed of according to the waste streams defined in the facility hazardous waste management procedures, Attachment B, Chemical Hygiene Plan, Section WS002, Table 1, current edition.

15.2. Samples and other solutions containing high concentrations of toxic materials must be disposed of according to the facility hazardous waste management procedures, Attachment B of the Chemical Hygiene Plan, Section WS003, Disposal of Samples After Analysis, current edition.

16. REFERENCES

16.1. Chemical Hygiene Plan, Attachment B, Hazardous Waste Management Procedures, current edition.

16.2. Document Number DFLM 01.0, including Revision DFLM 01.1 (September 1991).

16.3. Update of Toxicity of Equivalency Factors (TEFs) for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs/CDFs), EPA 625/3-89/016 (March 1989).

16.4. SW-846, Method 8280A, Update III, December 1996.

17. MISCELLANEOUS

17.1. Deviations from reference method(s).

17.1.1. The levels of pentachlorinated dioxins and furans are at 0.25, 0.625, 1.25, 2.5 and 5.0 in the calibration solutions as opposed to the method specified levels of 0.1, 0.25, 0.5, 1.0 and 2.0. (See TABLE 4) This adjustment aligns the calibration solutions with the CRQLs.

17.1.2. The levels of the hexa- to heptachlorinated isomers were adjusted from 1.25 ng/µL to 0.5 ng/µL in the window defining mixture. (See TABLE 6)

17.1.3. Tridecane was replaced with tetradecane.

17.1.4. The stock solution concentrations and volumes added to extracts were adjusted for ease of application.

17.1.5. NaCl and KOH were replaced with deionized water and NaOH for the acid-base washing procedure.

17.2. List of other SOPs cross-referenced in SOP.

17.3. Facility-specific information required to implement SOP.

17.4. Record Management and Documentation. (Sample bench sheets, logbook pages, data review checklists, etc.).

TABLE 1

Target Compound List (TCL) and Contract Required Quantitation Limits① (CRQL)

PCDD/PCDF	CAS Number	Water (ng/L)	Soil (µg/Kg)	Fly Ash (µg/Kg)	Chemical Waste② (µg/Kg)
2,3,7,8-TCDD	1746-01-6	10	1.0	1.0	10
2,3,7,8-TCDF	51207-31-9	10	1.0	1.0	10
1,2,3,7,8-PeCDF	57117-41-6	25	2.5	2.5	25
1,2,3,7,8-PeCDD	40321-76-4	25	2.5	2.5	25
2,3,4,7,8-PeCDF	57117-31-4	25	2.5	2.5	25
1,2,3,4,7,8-HxCDF	70648-26-9	25	2.5	2.5	25
1,2,3,6,7,8-HxCDF	57117-44-9	25	2.5	2.5	25
1,2,3,4,7,8-HxCDD	39227-28-6	25	2.5	2.5	25
1,2,3,6,7,8-HxCDD	57653-85-7	25	2.5	2.5	25
1,2,3,7,8,9-HxCDD	19408-74-3	25	2.5	2.5	25
2,3,4,6,7,8-HxCDF	60851-34-5	25	2.5	2.5	25
1,2,3,7,8,9-HxCDF	72918-21-9	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDF	67562-39-4	25	2.5	2.5	25
1,2,3,4,6,7,8-HpCDD	35822-46-9	25	2.5	2.5	25
1,2,3,4,7,8,9-HpCDF	55673-89-7	25	2.5	2.5	25
OCDD	3268-87-9	50	5.0	5.0	50
OCDF	39001-02-0	50	5.0	5.0	50

① All CRQL values listed here are based on the wet weight of the sample.

② The matrices included are oils, stillbottoms, oily sludge, wet fuel oil, oil-laced soil, and surface water heavily contaminated with the above-mentioned matrices.

TABLE 2

Ions Specified for Selected Ion Monitoring for PCDDs/PCDFs

Analyte	**Quantitation Ions**		**M- [COCl]+**
TCDD	320	322	259
PeCDD	356	358	293
HxCDD	390	392	327
HpCDD	424	426	361
OCDD	458	460	395
TCDF	304	306	243
PeCDF	340	342	277
HxCDF	374	376	311
HpCDF	408	410	345
OCDF	442	444	379
Internal Standards			
13C-2,3,7,8-TCDD	332	334	---
13C-1,2,3,6,7,8-HxCDD	402	404	---
13C-OCDD	470	472	---
13C-2,3,7,8-TCDF	316	318	---
13C-1,2,3,4,6,7,8-HpCDF	420	422	---
Recovery Standards			
13C-1,2,3,4-TCDD	332	334	---
13C-1,2,3,7,8,9-HxCDD	402	404	---
Cleanup Standard			
^{37}Cl-2,3,7,8-TCDD	328	③	263
Polychlorinated Diphenyl Ethers			

Analyte	**Quantitation Ions**		**M- [COCl]+**
HxCDPE	376	---	---
HpCDPE	410	---	---
OCDPE	446	---	---
NCDPE	480	---	---
DCDPE	514	---	---

③ There is only one quantitation ion monitored for the cleanup standard.

TABLE 3

Relationship of Internal Standards to Analytes and Relationship of Recovery Standards to Analytes, Internal Standards and Cleanup Standard

Internal Standards vs. Analytes

13C-TCDD	13C-HxCDD	13C-OCDD	13C-TCDF	13C-HpCDF
TCDD	HxCDD	OCDD	TCDF	HxCDF
PeCDD	HpCDD	OCDF	PeCDF	HpCDF

Recovery Standards vs. Analytes, Internal Standards, and Cleanup Standard

13C-1,2,3,4-TCDD	13C-1,2,3,7,8,9-HxCDD
TCDD	HxCDD
TCDF	HxCDF
PeCDD	HpCDD
PeCDF	HpCDF
	OCDD
	OCDF
13C-2,3,7,8-TCDD	13C-1,2,3,6,7,8-HxCDD
13C-2,3,7,8-TCDF	13C-1,2,3,4,6,7,8-HpCDF
^{37}Cl-2,3,7,8-TCDD	13C-OCDD

TABLE 4

Concentration Calibration Solutions

Analyte	CC1	CC2	CC3	CC4	CC5
2,3,7,8-TCDD	0.1	0.25	0.5	1.0	2.0
2,3,7,8-TCDF	0.1	0.25	0.5	1.0	2.0
1,2,3,7,8-PeCDF	0.25	0.625	1.25	2.0	5.0
1,2,3,7,8-PeCDD	0.25	0.625	1.25	2.0	5.0
2,3,4,7,8-PeCDF④	---	---	1.25	---	---
1,2,3,4,7,8-HxCDF④	---	---	1.25	---	---
1,2,3,6,7,8-HxCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,7,8-HxCDD④	---	---	1.25	---	---
1,2,3,6,7,8-HxCDD	0.25	0.625	1.25	2.5	5.0
13C-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5
^{37}Cl-2,3,7,8-TCDD④	---	---	0.25	---	---
1,2,3,4,7,8,9-HpCDF④	---	---	1.25	---	---
1,2,3,4,6,7,8-HpCDF	0.25	0.625	1.25	2.5	5.0
1,2,3,4,6,7,8-HpCDD	0.25	0.625	1.25	2.5	5.0
OCDD	0.5	1.25	2.5	5.0	10.0
OCDF	0.5	1.25	2.5	5.0	10.0
13C-2,3,7,8-TCDD	0.5	0.5	0.5	0.5	0.5
13C-2,3,7,8-TCDF	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,6,7,8-HxCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,4,6,7,8-HpCDF	1.0	1.0	1.0	1.0	1.0

Analyte	CC1	CC2	CC3	CC4	CC5
13C-OCDD	1.0	1.0	1.0	1.0	1.0
13C-1,2,3,4-TCDD	0.5	0.5	0.5	0.5	0.5
13C-1,2,3,7,8,9-HxCDD	0.5	0.5	0.5	0.5	0.5
^{37}Cl-2,3,7,8-TCDD④	---	---	0.25	---	---

④ Do not perform %RSD calculations on these analyses; however, these compounds are added to every calibration solution.

All concentrations are in ng/µL

TABLE 5

Criteria for Isotopic Ratio Measurements for PCDDs/PCDFs

Analyte	Selected Ions	Theoretical Ion Abundance	Control Limits
TCDD	320/322	0.77	0.65-0.89
PeCDD	356/358	1.55	1.32-1.78
HxCDD	390/392	1.24	1.05-1.43
HpCDD	424/426	1.04	0.88-1.20
OCDD	458/460	0.89	0.76-1.02
TCDF	304/306	0.77	0.65-0.89
PeCDF	340/342	1.55	1.32-1.78
HxCDF	374/376	1.24	1.05-1.43
HpCDF	408/410	1.04	0.88-1.20
OCDF	442/444	0.89	0.76-1.02
Internal Standards			
13C-2,3,7,8-TCDD	332/334	0.77	0.65-0.89
13C-1,2,3,6,7,8-HxCDD	402/404	1.24	1.05-1.43
13C-OCDD	470/472	0.89	0.76-1.01
13C-2,3,7,8-TCDF	316/318	0.77	0.65-0.89
13C-1,2,3,4,6,7,8-HpCDF	420/422	1.04	0.88-1.20
Recovery Standards			
13C-1,2,3,4-TCDD	332/334	0.77	0.65-0.89
13C-1,2,3,7,8,9-HxCDD	402/404	1.24	1.05-1.43

TABLE 6

PCDD/PCDF Isomers in the Window Defining Mix for A 60M DB-5 (or equivalent) Column

Homologue	First Eluted	Last Eluted	Approximate Concentration (ng/µL)
TCDD	1,3,6,8-	1,2,8,9-	0.5
TCDF	1,3,6,8-	1,2,8,9-	0.5
PeCDD	1,2,4,7,9-	1,2,3,8,9-	0.5
PeCDF	1,3,4,6,8-	1,2,3,8,9-	0.5
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-	0.5
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-	0.5
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-	0.5
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	0.5

TABLE 7

Matrix Spiking Solution

Analyte	Concentration (ng/µL)
2,3,7,8-TCDD	0.5
2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDF	1.25
1,2,3,7,8-PeCDD	1.25
1,2,3,6,7,8-HxCDF	1.25
1,2,3,6,7,8-HxCDD	1.25
1,2,3,4,6,7,8-HpCDF	1.25
1,2,3,4,6,7,8-HpCDD	1.25
OCDD	2.5
OCDF	2.5

This solution is prepared in isooctane (or nonane) and diluted with acetone prior to use. Only the ten isomers listed above will be used for evaluation. All seventeen 2,3,7,8-substituted isomers are incorporated into the matrix spike solution.

TABLE 8

Internal Standard, Recovery Standard, and Cleanup Standard Solutions

Internal Standards	**Stock Solution Concentration (ng/L)**	**Vol. Added to Sample (µL)**	**Final Amount (ng)**
13C-2,3,7,8-TCDD	0.5	100	50
13C-2,3,7,8-TCDF	0.5	100	50
13C-1,2,3,6,7,8-HxCDD	0.5	100	50
13C-1,2,3,4,6,7,8-HpCDF	1.0	100	100
13C-OCDD	1.0	100	100
Recovery Standards	**Concentration (ng/µL)**	**Vol. Added to Sample (µL)**	**Final Amount (ng)**
13C-1,2,3,4-TCDD	0.5	50	25
13C-1,2,3,7,8,9-HxCDD	0.5	50	25
Cleanup Standard	**Concentration (ng/µL)**	**Vol. Added to Extract (µL)**	**Final Amount (ng)**
^{37}Cl-2,3,7,8-TCDD	0.25	100	25

TABLE 9

Example Analytical Sequences

Time	Analysis
	Window Defining Mix
	Column Performance Solution (SP-2331)
Hour 0	CC3
	CC1 (Initial Calibration)
	CC2
	CC4
	CC5
	Blanks and Samples
Within 12 hour period	CC1
Hour 12	Column Performance Solution (SP-2331)
	CC3
	Blanks and Samples
Within 12 hour period	CC1
Hour 24	Column Performance Solution (SP-2331)
	CC3
	Blanks and Samples
	etc...
End of sequence	CC1

TABLE 10

Operating Conditions Guidelines	
Column Coating	DB-5 (or SP-2331)
Film Thickness	0.25 µm
Column Dimensions	60 m x 0.32 mm
Helium Linear Velocity	35-40 cm/sec at 240°C
Initial Temperature	170°C
Initial Time	5 min.
Temperature Program	increase to 310°C at 4°C/min.
Hold Time	until OCDF elutes

APPENDIX I

List of Analytes and Detection Limits

Analyte	Soil MDL	Water MDL
2,3,7,8-TCDF	See QAMP facility appendix.	
2,3,7,8-TCDD		
1,2,3,7,8-PnCDF		
2,3,4,7,8-PnCDF		
1,2,3,7,8-PnCDD		
1,2,3,4,7,8-HxCDF		
1,2,3,6,7,8-HxCDF		
1,2,3,7,8,9-HxCDF		
2,3,4,6,7,8-HxCDF		
1,2,3,4,7,8-HxCDD		
1,2,3,6,7,8-HxCDD		
1,2,3,7,8,9-HxCDD		
1,2,3,4,6,7,8-HpCDF		
1,2,3,4,7,8,9-HpCDF		
1,2,3,4,6,7,8-HpCDD		
OCDF		
OCDD		

APPENDIX II

Operating Instruction for the Finnigan - Mat. 4500

I. System Check-Out and Startup

A. Vacuum

1. High vacuum should be in the 10^{-6} to 10^{-8} range with a capillary column installed and all other gases shut off.

2. Normal column head pressure should be 08-12 psi for 30m narrow bore columns and 18-20 psi for 60m wide bore columns.

B. Temperatures

1. Manifold temperature: 100°C

2. Transfer line temperature: This temperature should be set high enough to allow the last eluting compound to have good peak shape. Approximate temperatures at 10°C above the final column temperature.

3. Ion source temperature: 150°C, LED blinking

C. RF Generator

1. Verify that all lights are on for various power supplies.

2. Depress multiple mass maker button on scope module. Check that these mass markers extend to the full range.

D. Tuning

1. Place the GC/MS in the manual mode by entering SS, type: EM1, FI1 and CA1 to turn on multiplier, filament, and cal gas.

2. Check to see if the following conditions are met:

a) Filament: ON

b) EM voltage/DS: ON

c) Dynode: ON

d) Helium GC Carrier: ON

e) Cal Gas: ON

f) Vacuum Protect: ON

g) Interface Power: ON

h) MS/MS Control Module: ON

3. Set up the GC/MS with m/z 219 and m/z 502 on the split screen.

4. Tune for the following:

a) Peak shape

b) Resolution

c) Peak intensities

d) Using the Quad offsets, offset programs, lenses and magnet

II. System Shutdown

A. Check to see that the following conditions are met:

1. Filament: OFF

2. EM voltage/DS: STBY

3. Dynode: ON

4. Helium GC Carrier: ON

5. Cal Gas: OFF

6. Vacuum Protect: ON

7. Interface power: ON

8. MS/MS Control Module: ON

APPENDIX III

Basic Maintenance

I. Removal of the Ion Source

A. Venting the Manifold

1. Turn the filament OFF; the dynode and multiplier to STBY

2. Turn the ionizer heater OFF by dialing in 00 on the thumbwheel switches. Allow the ionizer to cool about 0.5 hour.

3. Turn the Vacuum Protect and Ion Gauge OFF

4. Turn OFF the turbos; then the mechanical pumps.

5. Insert the backfill plug assembly into the solid inlet port.

6. Open the solids inlet valve and wait for the pressure to equalize.

B. Loosen the O-ring fitting on the inlet evacuation solenoid and disconnect the ionizer cable and cal gas cables from the front flange assembly.

C. Loosen and remove all but the top one of the flange bolts.

D. Holding the front flange firmly, remove the last flange bolt.

E. Looking through the viewing port, remove the source, being careful not to scrape it against the transfer line.

II. Steps to Cleaning the Source

A. Refer to pages 6-3 through 6-9 in the 4500 series GC/MS operators manual.

III. Installation of the Ion Source

A. Check to see that the copper gasket is in good condition. If not, replace it.

B. Check with an ohmmeter that the lens leads are not touching each other.

C. Slip the O-ring nut and O-ring over the inlet evacuation line.

D. Carefully take the ionizer flange assembly in two hands and insert the ionizer into the vacuum manifold. Looking through the viewing port, guide the flange into place.

E. Put in the bolts and hand-tighten.

F. Wrench-tighten the bolts using the opposite bolt technique.

G. Fasten the inlet evacuation line to the solenoid.

H. Re-evacuating the manifold.

1. Turn on the mechanical pumps and turbomolecular pumps by pressing MECH Pumps and TURBO Pumps.

2. When the manifold fore pressure is reduce to at least 0.04 torr and the turbopump is at least 80%, start the ion gauge.

3. With the ion gauge operating, place the system in the protect mode by pressing the VACUUM PROTECT button.

IV. Removing the Ion Volume

A. Make sure that the filament and electron multiplier are OFF.

B. Make sure that the release knob in the handle of the insertion/removal (I/R) tool is retracted and locked.

C. Insert the tip of the tool into the vacuum seal at the entrance of the solids inlet valve, with the guide pin in the groove of the guide bar.

D. Slide the tool in until the guide pin reaches the first step in the guide bar.

E. Tighten the seal by rotating the black vacuum seal nut clockwise until finger tight.

F. Evacuate the solids inlet valve by depressing the INLET EVAC push button on the vacuum controller.

G. Set the FOREPRESSURE switch to INLET.

H. Monitor the inlet pressure, and when it is reduced to 0.05 torr (after 5 or 10 seconds) disengage the INLET EVAC push button.

I. Open the solids inlet valve by rotating the handle fully counterclockwise.

J. Slowly slide the I/R tool collet all the way into the ion volume adapter.

K. Pull the release knob away from the handle and let it slide forward to expand the collet inside the adapter.

L. Slowly and carefully withdraw the I/R tool, with ion volume assembly attached until the guide pin reaches the offset stop.

M. Close the solids inlet valve by turning the handle fully clockwise.

N. Loosen the vacuum seal nut, rotate the pin past the offset stop, and withdraw the tool.

O. Release the ion volume by pulling back the release knob until it locks in the handle of the tool. Using clean gloves (or tweezers if it is hot), place the ion volume in the storage box provided. Close the lid to keep out dust.

V. Installing the Ion Volume

A. Ensure that the release knob is retracted and insert the collet end of the I/R tool into the adapter of the selected ion volume assembly.

B. Pull the release knob out and let it go forward so as to expand the collet. Be sure that the adapter is fully seated on the collet and that the alignment bracket orientation is correct. The forks on the alignment bracket should be on the spring near the collar of the adapter.

C. Insert the I/R tool with the ion volume assembly through the solids inlet valve as described in Section IV.

D. Carefully slide the tool through the solids inlet valve, stopping about 20 mm short of complete insertion.

E. Look through the window on the top of the manifold and make sure the collector hole is pointing straight up.

F. Slowly slide the I/R tool the rest of the way in and check the proper seating of the ion volume assembly. If it is not properly seated, slide the I/R tool back about 20 mm and make sure that the collector hold is up and the detent flats down, and the ion volume does not seat properly, it usually means there is an alignment problem.

G. Retract and lock the release knob (close the collet) and remove the tool as directed in Section IV.

H. Store the I/R tool in the accessory rack on the side of the instrument.

VI. Column Installation

A. Bring the manifold to atmospheric pressure in Section I.A. and cool the injector and transfer line.

B. Uncoil a few turns of both ends of the column from its cage.

C. Using a diamond pencil, score, and break about 6 inches from each of the sealed ends of the column.

D. Mount the on its cage inside the GC oven, and slide a 1/16 in. Swagelok nut and graphite ferrule onto the front end of the column.

E. Again, using a diamond pencil, score and break about 1 inches from the front end to ensure that no pieces of the ferrule are inside the column.

F. Insert the fused-silica capillary column into the bottom of the injector 55-60 mm.

G. Attach the 1/16 inch Swagelok nut and tighten finger-tight first, then tighten with a 5/16 inch wrench.

H. For a 30m x 0.25 mm ID fused-silica capillary column, set the column head pressure, using the pressure regulator on the front panel, to 8-12 psi. For a 60m x 0.32 mm ID, set the head pressure to 18-20 psi.

I. Using a bubble flow meter, adjust the SWEEP ADJUST valve on the front of the GC to 5 cc/min. and adjust the SPLIT ADJUST valve to 75 cc/min.

J. Slide a 1/16 inch Swagelok nut and a graphite vespel onto the detector end of the column.

K. Using a diamond pencil, score, and break about 1 inch off the end of the column to ensure that no pieces of the ferrule get into the column.

L. Using a flashlight, look through the vacuum view port and thread the column through the transfer-line to the point where it appears out the end of the transfer-line nozzle.

M. Now, thread the column to the entrance of the source block.

CAUTION: If the column is inserted too far into the source block, it will be shaved off by insertion or removal of the ion volume. This piece could end up in the instrument's vacuum system.

N. Attach the 1/16 inch Swagelok, tighten with a 5/16 inch wrench, and bring the system back to high vacuum as in Section III.H.

FIGURE 1

FIGURE 2